National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2036

Near-Infrared Wavelength/Wavenumber Reflection Standard

This Standard Reference Material (SRM) is a certified transfer standard intended for the verification and calibration of the wavelength/wavenumber scale of Near-Infrared (NIR) spectrometers operating in diffuse reflectance mode. SRM 2036 is a glass that is compositionally identical to SRM 2065 *Ultraviolet-Visible-Near–Infrared Transmission Wavelength/Wavenumber Standard* physically contacted with a piece of sintered polytetrafluoroethylene (PTFE). The combination of the rare earth oxide glass with a nearly ideal diffuse reflector provides reflection-absorption bands that range from approximately 15 % R to 40 % R. SRM 2036 is certified for the 10 % band fraction centroid of seven bands spanning the spectral region from 975 nm to 1946 nm (air wavelength). In addition, it is certified for the 10 % band fraction centroid location of the same seven bands in the spectral region from 10 300 cm^{-1} to 5 130 cm^{-1} at 8 cm^{-1} resolution (vacuum wavenumber).

The glass is a mixture of 3.00 mole % holmium oxide (Ho_2O_3), 1.30 mole % samarium oxide (Sm_2O_3), 0.68 mole % ytterbium oxide (Yb_2O_3), and 0.47 mole % neodymium oxide (Nd_2O_3) in a matrix containing oxides of lanthanum (La_2O_3), boron (B_2O_3), silicon (SiO_2), and zirconium (ZrO_2). The optical filter is 25 mm in diameter and 1.5 mm thick. The sintered PTFE is 25 mm in diameter and approximately 6 mm thick. A unit of SRM 2036 consists of the optical filter-PTFE assembly mounted in an optical holder, contained in a wooden box.

Certification: The certified reflection-absorption band locations for SRM 2036 are given in Tables 1 and 2 of this certificate.

Expiration of Certification: The certification of this SRM is valid, within the measurement uncertainties specified, until **30 April 2009**, provided the SRM is handled and stored in accordance with the instructions given in this certificate. However, the certification is nullified if the SRM is damaged, disassembled, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

The overall direction and coordination of the technical measurements leading to the certification of SRM 2036 were provided by S.J. Choquette and G.W. Kramer of the NIST Analytical Chemistry Division.

The production and certification of SRM 2036 was conducted by S.J. Choquette of the NIST Analytical Chemistry Division with assistance from L.M. Hanssen and E.A. Early of the NIST Optical Technology Division.

The SRM filter glass was cut and polished by J. Fuller of the NIST Fabrication Technology Division.

Statistical consultation was provided by J.J. Filliben of the NIST Statistical Engineering Division and D.L. Duewer of the NIST Analytical Chemistry Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald of the NIST Measurement Services Division.

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Measurement Conditions: The diffuse reflectance certification measurements for the NIR spectral region (10 300 cm^{-1} to 5 130 cm^{-1}) were made using Bruker IFS66 and Bio-Rad FTS-60 Fourier transform (FT) spectrometers.[1] The IFS66 spectrometer was equipped with a bifurcated-fiber-optic-diffuse-reflectance probe. The FTS-60 spectrometer was equipped with a custom integrating sphere assembly that enabled the measurement of the total (8º sampling geometry) and diffuse components of the reflectance spectrum of SRM 2036. Details about this spectrometer can be found in References 1 and 2. The IFS66 spectrometer calibration was validated with ambient water vapor bands, SRM 2065, and SRM 1920a *Near Infrared Reflectance Wavelength Standard from 740 nm to 2000 nm*. The FTS-60 spectrometer was calibrated using ambient water vapor and carbon dioxide bands.

The dispersive air-wavelength NIR measurements were performed on a PerkinElmer® Lambda 900 (PE900) spectrometer equipped with a 60 mm integrating sphere and a Cary 5e spectrometer equipped with a 110 mm integrating sphere assembly. Both spectrometers were used to measure the total and diffuse components of this standard. The air-wavelength axis of the PE900 spectrometer was calibrated in the NIR using the emission lines of the internal deuterium lamp (second order of the grating), calibration runs of SRM 2065 in transmittance and SRM 1920a in diffuse reflectance. The Cary 5e was calibrated using the same emission lines and standards as the PE900.

The transmission spectra of the optical glass only (without the PTFE backing) were measured on the IFS66 spectrometer operated in transmission mode. SRM 2036 is **NOT** intended for use as a transmission wavelength/wavenumber standard. However, the homogeneity of this melt and similarity of its band positions to SRM 2065 were determined using transmission measurements. For these transmission measurements, the IFS66 was calibrated in vacuum wavenumber units using SRM 2517 *Wavelength Reference Absorption Cell-Acetylene* [3]. The calibration of the spectrometer was validated using water vapor bands.

Details of the measurements and data analysis for both FT and dispersive measurements can be found in References 4 and 5.

Certified Values: The certified [6] vacuum wavenumber locations for the seven reflection-absorption bands spanning the range from 10 300 cm^{-1} to 5 130 cm^{-1} are listed in Table 1. These values were obtained at 8 cm^{-1} constant wavenumber resolution and are certified for operation between 21 °C and 26 °C. The certified values represent the mean band locations from both the IFS66 fiber probe measurements and the FTS-60 total and diffuse-component-only measurements. The location bias for each of these modes of operation is well within the short-term precision variance of these instruments operated in diffuse reflectance. Atmospheric water vapor is a significant source of variance for band 3, and this band should be used with caution when calibrating unpurged commercial spectrometers with SRM 2036.

The certified values for the NIR air wavelength band locations for the seven reflection-absorption bands from 976 nm to 1946 nm for 3 nm, 5 nm, and 10 nm spectral slit width (SSW) resolution at 21 °C are listed in Table 2. The certified values of the air wavelength band locations represent the mean band locations from both the Cary 5e and PE900 spectrometers operated in both total and diffuse only collection geometries. As for the FT measurements, the location bias for each of these modes of operation of the SRM was within the short-term precision variance of the dispersive spectrometers used for certification of this standard. The NIR reflectance spectrum of SRM 2036 is illustrated in Figure 1.

Information Values: Information values for the NIR vacuum wavelength temperature coefficients and 0 °C intercepts are given in Table 3. SRM 2036 has additional absorbance bands between 334 nm and 1000 nm. The locations of these bands are currently uncertified. Information values on the location of these bands are provided in Table 4 for a SSW of 5 nm. The ultraviolet-visible reflectance spectrum of SRM 2036 is illustrated in Figure 2.

Wavenumber and Wavelength Band Location Methodology: The method used to determine the certified NIR wavenumber (ν) and wavelength (λ) band locations of SRM 2036 is the centroid (center-of-gravity) technique [7,8,9]. If another technique is used, a comparison with the certified values **may not be valid**. In this certificate, positions determined with the centroid algorithm are referred to as *band* locations. For SRM 2036 centroid calculations, a 10 % fraction of the band was used for both wavenumber and wavelength reflection-absorption data. Further information on the use of this algorithm with other SRM's can be found in Reference 9.

[1]Certain commercial equipment is identified to specify adequately the experimental procedure. Such identification does not imply a recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment is the best available for the purpose.

Certification Uncertainty: The expanded uncertainty (U_{95}) for the wavenumber and wavelength band locations given in Tables 1 and 2 are determined from the appropriate combination of component standard uncertainties (i.e. estimated standard deviations), with a coverage factor based on Student's *t*-distribution, to define the interval within which the unknown value of the band can be asserted to lie with a level of confidence of approximately 95 % [10]. Components of the uncertainty for the vacuum wavenumber band locations include: instrument bias (two certification spectrometers), calibration of the NIST FT spectrometers, location shift due to temperature, water vapor interference, and the short term precision variance. Components of the uncertainties for the air wavelength band locations include: instrument bias (two reference instruments) and the location uncertainty of the wavelength calibration standards.

Handling and Storage: When not in use, SRM 2036 should be stored in the provided box in a clean location. Airborne particles, aromatics, and improper handling may adversely affect the PTFE diffuser surface. Care should be taken when handling the SRM to prevent fingerprints on the surface of the glass or the PTFE reference. The diffuser cannot be cleaned without adversely affecting the surface, except by using a clean air bulb to gently remove dust. The glass surface may be cleaned with lint free tissue paper and dry methanol using standard techniques for cleaning laser optics.

INSTRUCTIONS FOR USE

SRM 2036 is intended for the calibration of diffuse reflectance spectrometer accessories. The method for use will vary with the type of accessory. A reference spectrum may be obtained from the exposed PTFE portion of the SRM or an equivalent reference. The sample spectrum is acquired from the rare-earth-oxide-glass side of this SRM. The reflectance spectrum of the standard is then calculated as the ratio of the sample to the reference spectrum. For air wavelength measurements, the data spacing should be 0.5 nm per data point or less. For vacuum wavenumber measurements, the data spacing should be 1.0 cm^{-1} per data point or less. These data spacings ensure that the centroid location method itself does not contribute significantly to the location bias. Correction to absolute reflectance or for specular reflectance is not necessary as the bias for these is included in the location uncertainties. However, the front surface Fresnel reflection of the SRM may give reflectance values exceeding 100 % especially with fiber probes when referenced to the bare PTFE reference. This will not affect the band location estimates within the stated uncertainties.

Measurement of the SRM under a dry nitrogen purge is highly recommended. If a nitrogen purge is not available, the locations of band 1 and band 3 may differ from the certified values. Acquire the reflectance spectrum, at a temperature of 23 °C ± 3 °C. Compare each measured band location to its certified value listed in Table 1 or Table 2. Band locations in Table 1 are vacuum-wavenumber values, while those in Table 2 are air-wavelength values. Taking into account the certification uncertainty of each band of SRM 2036, any statistically significant differences between the measured and certified band locations may then be used to recalibrate the spectrometer wavenumber/wavelength scale.

Table 1. Certified[a] Band Locations[b] and Uncertainties[c] for SRM 2036
Vacuum Wavenumber at 8 cm^{-1} Resolution

Band	Centroid Location cm^{-1}	$\pm U_{95}$ cm^{-1}
1	5139.4	0.34
2	6803.9	0.94
3	7312.7	0.61
4	8179.0	0.36
5	8682.0	1.65
6	9293.9	1.30
7	10244.9	0.70

Table 2. Certified[a] Band Locations[b] and Uncertainties[c] for SRM 2036, Air Wavelength

	Spectral Slit Width					
	3 nm		5 nm		10 nm	
	Centroid Location	$\pm U_{95}$	Centroid Location	$\pm U_{95}$	Centroid Location	$\pm U_{95}$
Band	nm	nm	nm	nm	nm	nm
7	976.0 (0.02)[d]	0.3	976.0 (0.01)	0.2	975.9 (0.01)	0.6
6	1075.7 (0.01)	0.2	1075.7 (0.01)	0.9	1075.8 (0.03)	2.2
5	1151.4 (0.01)	0.1	1151.2 (0.01)	1.0	1151.0 (0.01)	3.4
4	1222.1 (0.02)	0.4	1222.1 (0.01)	0.3	1222.1 (0.03)	0.9
3	1367.1 (0.01)	0.4	1367.2 (0.01)	0.5	1367.3 (0.02)	0.2
2	1469.6 (0.02)	0.4	1469.6 (0.02)	1.7	1469.5 (0.03)	3.7
1	1945.7 (0.04)	0.3	1945.8 (0.02)	0.7	1945.6 (0.01)	1.5

[a] A NIST *Certified Value* represents data reported on an SRM Certificate for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been fully investigated or accounted for by NIST. The 8 cm^{-1} constant wavenumber band locations are certified, as are the 3 nm, 5 nm, and 10 nm air wavelength locations.

[b] Band location determined using a centroid method with a band fraction of 0.1; see Figure 1 for band identification.

[c] Uncertainties are expressed as U_{95}, the expanded uncertainty calculated in accordance with reference 8. A $\pm U_{95}$ provides an approximate 95 % confidence interval about the certified value.

[d] The number in parenthesis is the standard error of the mean centroid band location in nanometers. The $\pm U_{95}$ of the air wavelength bands of SRM 2036 is determined by the uncertainty of the calibration of the reference instruments with SRM 2065.

Table 3. Temperature Coefficients for SRM 2036: Parameters and Uncertainties for 4 cm^{-1} Resolution Spectra[a]

Band	β_i $cm^{-1}/°C$ [b]	α_i cm^{-1} [b]
1	-0.0494(15)	5139.77(12)
2	0.0878(16)	6802.16(5)
3	0.012(6)	7312.41(12)
4	0.0597(10)	8176.78(6)
5	-0.0395(15)	8682.5(2)
6	-0.0751(19)	9295.84(15)
7	0.0179(7)	10245.12(3)

[a] All band locations can be described by a band-specific linear model: $b_i = \alpha_i + \beta_i T$, where b_i denotes the estimated band location, T is the temperature in °C of the filter during acquisition of the spectrum, β_i is the change in band location per °C (temperature coefficient slope) for the i^{th} band, and α_i is the extrapolated location of the band at zero °C (temperature coefficient intercept).

[b] The digits in parentheses denote the combined standard uncertainty units of the last reported digit of the coefficient.

Table 4. Information[a] Band Locations for SRM 2036 Measured in Reflectance at 5 nm SSW

Band	Wavelength (nm)
20	333.8
19	346.1
18	361.3
17	374.3
16	385.8
15	402.6
14	418.2
13	485.3
12	538.2
11	583.3
10	642.7
9	747.6
8	804.2

[a] A NIST information value is a non-certified value with no uncertainties reported as there is insufficient information to make an assessment of the uncertainties.

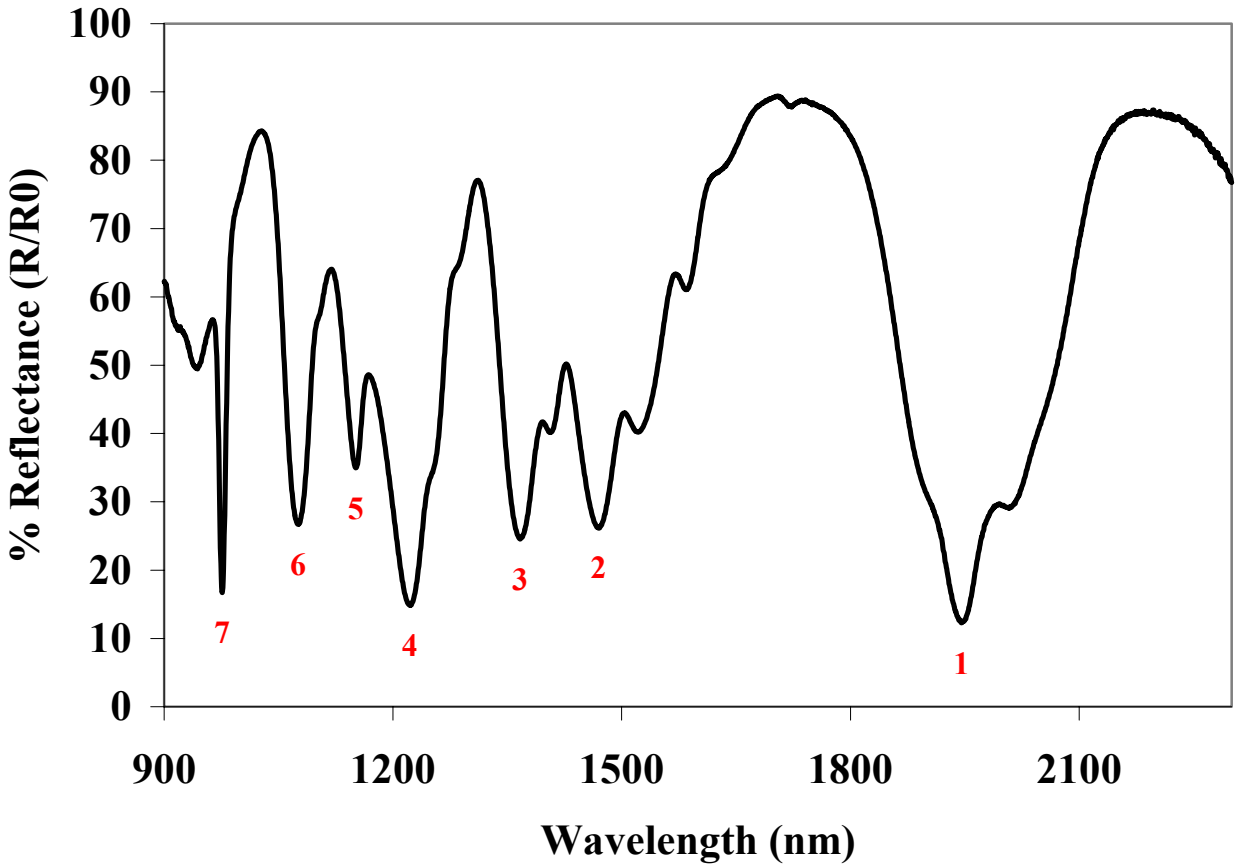

Figure 1. SRM 2036 Diffuse Reflectance Spectrum. Specular-Excluded Spectrum Acquired at 5 nm Spectral Slit Width

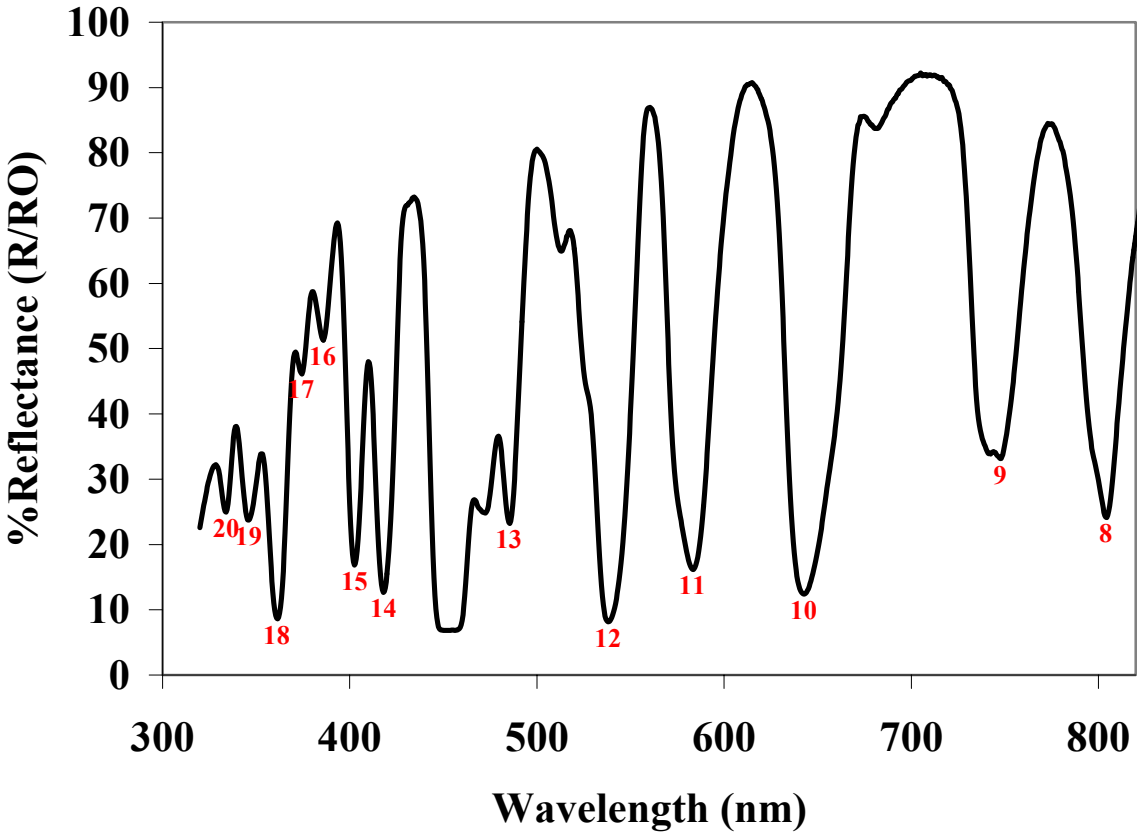

Figure 2. SRM 2036 Diffuse Reflectance Spectrum. Specular-Included Spectrum Acquired at 5 nm Spectral Slit Width

REFERENCES

[1] Hanssen, L.M.; S.G. Kaplan; *Infrared Diffuse Reflectance Instrumentation and Standards at NIST*; Anal. Chim. Acta**,** Vol. 380, pp. 289-302 (1998).

[2] Hanssen, L.M.; Integrating Sphere System and Method for Absolute Measurement of Transmittance, Reflectance and Absorptance of Specular Samples; Appl. Opt., Vol 40, pp. 3196-3204 (2001).

[3] Gilbert, S.L.; Swann, W.C.; *Standard Reference Materials: Acetylene C_2H_2 Absorption Reference for 1510 nm – 1540 nm Wavelength Calibration-SRM 2517*; NIST Special Publication 260-133 (1997).

[4] Duewer, D.L.; Choquette, S.J.; O'Neal L.E.; Filliben, J.J.; *Rare-Earth Glass Reference Materials for Near-Infrared Spectrometry: Sources of X-Axis Location Variability*; Anal. Chim. Acta.

[5] Choquette, S.J.; O'Neal, L.E.; Duewer, D.L.; *Rare-Earth Glass Reference Materials for Near-Infrared Spectrometry: Correcting and Exploiting Temperature Dependencies*; Anal. Chem., Vol. 75, pp. 961-966 (2003).

[6] May, W.; Parris, R.; Beck, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Gettings, R.; MacDonald, B.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurement*; NIST Special Publication 260-136 (2000).

[7] Cameron, D.G.; Kauppinen, J.K.; Moffat, J.K.; Mantsch, H.H.; *Precision in Condensed Phase Vibrational Spectroscopy*; Appl. Spectrosc. Vol. 36, pp. 245-250 (1982).

[8] Zhu, C.; Hanssen, L.M.; *Studies of Polystyrene Wavenumber Standard for Infrared Spectrometry*; 11th International Conference of Fourier Transform Spectrometry, AIP Proceedings, Vol. 430, Ed. J.A. de Haseth; pp. 491-494, American Institute of Physics, NY (1998).

[9] *Standard Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests*; Annual Book of Standards 2000, Vol. 3.06, section three, Analytical Procedures, E1421-99.

[10] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed., ISO, Geneva, Switzerland, (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at http://physics.nist.gov/Pubs/.

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.